

Mr. Eric Winiecki
EPA Project Coordinator
U.S. Environmental Protection Agency, Region 10
1200 Sixth Avenue, Suite 900
Seattle, WA 98101

Subject:

DOCKET NO. SDWA-10-2013-0080 – Yakima Valley Dairies
Request for Modification
Application Field Management Plan
Analyze Soil Ammonium (NH_4^+) in place of Soil Ammonia (NH_3)

Dear Mr. Winiecki:

ARCADIS U.S., Inc. (ARCADIS), on behalf of: (1) Cow Palace, LLC; (2) D & A Dairy, LLC (also known as D&A Dairy L.L.C.), George DeRuyter & Son Dairy, L.L.C., and George & Margaret, L.L.C; and (3) Liberty Dairy LLC and its associated dairy facility H&S Bosma Dairy, makes this request to U.S. Environmental Protection Agency (EPA) for a modification to the Yakima Valley Dairies (YVD) Consent Order (CO) Statement of Work (SOW), as provided under Section 45 of the CO.

During negotiation of the YVD SOW, ARCADIS and U.S. Environmental Protection Agency (EPA) technical representatives raised concerns regarding the analysis of ammonium (NH_4^+) for the application field soils. EPA originally proposed that soil ammonium be analyzed for application field samples collected under SOW Section III.F.1. The discussions between ARCADIS and EPA led to agreement that an acceptable analytical method was not available to quantify soil ammonium and that soil ammonia (NH_3) would be analyzed as an alternative. Ammonia was stipulated as a soil analytical constituent in SOW Section III.A.3.b.

Following retention of the Agricultural Professional (AgriManagement, Inc.) by the YVD, discussions between ARCADIS and AgriManagement led to the determination that ammonium is the proper constituent to be analyzed when considering the following reactions and conditions as related to the nitrogen cycle process in agricultural soils :

Imagine the result

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Date:
May 16, 2013

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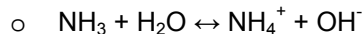
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SK030335.0001

- Aminization: $\text{Organic N} \rightarrow \text{R-NH}_2$

Microbial driven reaction (depends on temps, pH, organic matter, soil moisture, etc.).

- Ammonification: $\text{R-NH}_2 \rightarrow \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$

This is a microbial driven reaction. NH_3 is a gas that reacts very quickly with free hydrogen or water within soils to form ammonium (NH_4^+).



Alkaline conditions tend to push this reaction to the right. However, this natural process is almost entirely associated with surface applications of ammonium fertilizers and/or organic wastes.

This is the same process that occurs when anhydrous ammonia gas is injected into soils for fertilization. The NH_3 gas reacts with the water in the soil to quickly form NH_4^+ . If the soil is very dry or very wet, then some of the NH_3 gas will be lost to the environment but, under normal agricultural conditions, the NH_3 is retained as NH_4^+ which is held on soil exchange sites and not subject to loss from leaching. Being a gas, ammonia is not very stable within the soil system and will generally either escape into the atmosphere if on the soil surface or be quickly converted to ammonium below the soil surface.

- Nitrification: $\text{NH}_4^+ \rightarrow \text{NO}_3^-$

This is a two-step microbial process that occurs fairly quickly under conditions that are favorable for crop growth. While ammonium also is constantly in flux, being a cation, it can be retained within the profile where it can more easily be measured. Each soil will have a specific NH_4^+ equilibrium that will be generally maintained. This equilibrium level will vary depending upon soil pH, organic matter, soil moisture, temperature, crop, etc. Additions of ammonium-based fertilizers or animal wastes will push this level higher for a short period of time and crop removal can push it lower, but this change can be measured.

Based on these conditions, ARCADIS agrees with the initial EPA proposal that soil ammonium is measured for the application field soils. ARCADIS proposes replacing ammonia with ammonium in SOW Section III.A.3.b and the Application Field Management Plan(s). ARCADIS proposes analyzing for ammonium using Plant, Soil and Water Reference Methods for the Western Region Method S-3.50, Soil Ammonium Nitrogen Method, KCl Extraction / Exchangeable Ammonium (attached). ARCADIS makes this request in accordance with Section 45 of the YVD CO.

If you have any questions or comments, please do not hesitate to call. Thank you for your consideration of this request.

Sincerely,

ARCADIS U.S., Inc.



Kevin M. Freeman
YVD Project Coordinator

Attachments:

Method S-3.50, Soil Ammonium Nitrogen Method

Copies:

Scott Stephen, AgriManagment, Inc.

[REDACTED], Cow Palace LLC

[REDACTED], George DeRuyter & Son Dairy LLC

[REDACTED], Liberty Dairy LLC

Rene Fuentes, EPA

Jennifer MacDonald, EPA

Patrick W. Ryan, Perkins Coie LLP

Lori Terry Gregory, Foster Pepper PLLC

Scope and Application

This method involves the semiquantitative extraction of ammonium ($\text{NH}_4\text{-N}$) from soils using 2.0 N KCl. Ammonium is determined by spectrophotometric, diffusion-conductivity instruments or distillation techniques. The method doesn't quantitatively extract ammonium from mineral structures (i.e. nonexchangeable $\text{NH}_4\text{-N}$) or bound to organic compounds. The method is readily adapted to manual or automated techniques. The procedure outlined follows that outlined by Keeney and Nelson (1982) for determining nitrate nitrogen with a modification in which 25 mL of KCl and 5.0 g of soil are used instead of 100 mL and 10 g soil. Care must be taken to avoid contamination from filter paper and operator handling. Soil ammonium concentrations are generally low in mineral soils ($< 10 \text{ mg kg}^{-1}$). The method detection limit is approximately 0.2 mg kg^{-1} (on a dry soil basis) and is generally reproducible $\pm 7\%$.

Equipment

1. Analytical balance: 100.0 g capacity, resolution $\pm 0.01 \text{ g}$.
2. Repipette dispenser, calibrated to $25.0 \pm 0.2 \text{ mL}$.
3. Reciprocating horizontal mechanical shaker, capable of 180 oscillations per minute (opm).
4. Extraction vessels and associated filtration vessel.
5. Whatman No. 42 or equivalent highly retentive filter paper.
6. Spectrophotometer, or flow injection analyzer (FIA), or distillation instruments.

Reagents

1. Deionized water, ASTM Type I grade.
2. Potassium chloride extracting solution, 2.0 N KCl: Dissolve 150 g of reagent grade KCl in 500 mL deionized water and dilute to a 1000 mL (See Comment #1).
3. Standard calibration solutions of $\text{NH}_4\text{-N}$. Prepare six calibration standards ranging from 0.1 to 20.0 mg L^{-1} concentration, diluted in 2.0 N KCl extraction solution prepared from $1000 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ standard solution.

Procedure

1. Weigh $5.0 \pm 0.05 \text{ g}$ of air-dried soil pulverized to pass 10 mesh sieve ($< 2.0 \text{ mm}$) into extraction vessel. Add 25.0 mL of 2.0 N KCl extraction reagent using repipette dispenser (See Comment #2). Include a method blank.
2. Place extraction vessel(s) on reciprocating mechanical shaker for thirty (30) minutes.
3. Filter extract (See Comment #3), refilter if filtrate is cloudy (comment #4).
4. Ammonium-N content of the extract is determined using a spectrophotometer, diffusion-conductivity instruments or distillation techniques using standard calibration solutions (See Comment #4 and #5). The ammonium nitrogen content of the digest solution can be determined with a rapid flow analyzer (Technicon Method No. 334-74A/A) or a flow injection analyzer (FIA). This determination can also be made using the Kjeldahl distillation method. Adjust and operate instruments in accordance with manufacturer's instructions. Determine ammonium concentration of a method blank and unknown samples.

Calculation

$$\text{NH}_4\text{-N mg kg}^{-1} \text{ in soil} = (\text{NH}_4\text{-N mg L}^{-1} \text{ in filtrate} - \text{method blank}) \times 5$$

Report soil ammonium concentration to the nearest 0.1 mg kg⁻¹ (See Comment #6)

Comments

1. Soils may be extracted with 2.0 N KCl for the simultaneous determination of nitrate (Method 3.10).
2. Check repipette dispensing volume calibration using an analytical balance.
3. Check filter paper supply for possible contamination of and NH₄-N. If contamination is greater than 0.2 mg L⁻¹ on a solution basis, rinse filter paper with 2.0 N KCl.
4. It is recommended that soils extracted for ammonium be analyzed within two (2) hours after extraction.
5. Samples having ammonium concentrations exceeding the highest standard will require dilution and reanalysis.
6. Ammonium-nitrogen (NH₄-N) results can be expressed on a volume basis. Assuming the sample represents a 0-6 inch (0-15 cm) depth of the soil, then: NH₄-N mg kg⁻¹ × 2.0 ≅ NH₄-N lbs ac⁻¹

Literature

Bremner, J. M. and D. R. Keeney. 1965. Determination and isotopic ratio analysis of different forms of nitrogen in soils: I. Apparatus and procedure for distillation for and determination of ammonium. Soil Sci. Soc. Am. Proc. 29:504-507.

Dahnke, W. C. 1990. Testing soils for available nitrogen. p. 120-140. In: R. L. Westerman (ed.) Soil testing and plant analysis. Soil Sci. Soc. Am. Book series 3 ASA Madison WI.

Keeney, D. R. and D. W. Nelson. 1982. Nitrogen-inorganic forms. In A. L. Page (eds.) Methods of soil analysis, part 2. Agron. Monogr. 9, 2nd ed. ASA and SSSA, Madison, WI. p. 643-698.